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<b>(21) International Application Number:</b> PCT/US97/17268 <b>(22) International Filing Date:</b> 26 September 1997 (26.09.97) <b>(30) Priority Data:</b> 08/726,378      4 October 1996 (04.10.96)      US <b>(71) Applicant:</b> LIBBEY-OWENS-FORD CO. [US/US]; 811 Madison Avenue, Toledo, OH 43697 (US). <b>(72) Inventors:</b> PARKER, Anthony, A.; 4104 Wyndwood Court, Toledo, OH 43623 (US). STRICKLER, David, A.; 2339 Barrington Drive, Toledo, OH 43606 (US). PARK, Hung, S.; 306 Lear Road, Avon Lake, OH 44012 (US). <b>(74) Agent:</b> OBERLIN, Phillip, S.; Marshall & Melhorn, Four SeaGate, 8th floor, Toledo, OH 43604 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> COPOLYMERS OF VINYL CHLORIDE, ALLYL GLYCIDYL ETHER, A VINYL ESTER AND AN UNSATURATED ORGANIC TRIFUNCTIONAL SILANE		
<b>(57) Abstract</b>  An improved method is provided for copolymerizing vinyl chloride with allyl glycidyl ether and a vinyl ester. The copolymers so formed include 70-99 weight percent of vinyl chloride, 0.05-15 weight percent of allyl glycidyl ether, and 0.05-15 weight percent of a vinyl ester, preferably vinyl acetate. The copolymers of this invention can be compounded to provide films exhibiting improved heat stability, low haze, and good adhesion to solid surfaces such as glass and metal. The compounded resins thus obtained may be especially advantageously used in forming the interlayer of laminated safety glazings, such as vehicle windshields and architectural glazings. The copolymerization of vinyl chloride, allyl glycidyl ether, a vinyl ester and small amounts of an unsaturated organic trifunctional silane provide self-adhesion without gelation.		

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TITLE

5 COPOLYMERS OF VINYL CHLORIDE, ALLYL GLYCIDYL ETHER,  
A VINYL ESTER AND AN UNSATURATED ORGANIC TRIFUNCTIONAL  
SILANE

FIELD OF THE INVENTION

This invention relates to copolymers of vinyl  
chloride with allyl glycidyl ether and a vinyl ester.  
10 More particularly, the invention relates to a suspension  
polymerization process for polymerizing vinyl chloride  
with allyl glycidyl ether and a vinyl ester, preferably  
vinyl acetate, to produce a resin for forming films having  
good heat stability, low haze and good adhesion.

15 The additional copolymerization of very low amounts  
of an unsaturated organic trifunctional silane provides  
self-adhesion, low haze and no gelation.

SUMMARY OF RELATED ART

20 It is well known that vinyl chloride can be  
homopolymerized as well as copolymerized with numerous  
monomers. Those polymers have been widely used in various  
kinds of applications for many years. Over the years,  
many attempts have been made to improve the physical  
25 properties of these polymers. The incorporation of  
comonomers into vinyl chloride has often been aimed  
specifically at increasing the polymer's thermoplastic  
flow under processing conditions and improving the  
polymer's solubility characteristics, while retaining the  
30 toughness and generally good physical properties of the  
vinyl chloride homopolymers. Generally, the  
copolymerization of vinyl chloride has become an  
alternative means of reducing the severity of the

processing conditions needed to fabricate the resins into the desired final articles.

The copolymers of vinyl chloride with vinyl acetate comonomer are by far the most important commercial products among the vinyl chloride copolymers. The content of vinyl acetate typically ranges from about 3% to 20%, and the molecular weight can range from very low to moderately high. The higher the level of bound vinyl acetate, the greater the tendency for the colloids to destabilize during polymerization. These copolymers may be prepared by solution, emulsion, or suspension polymerization, depending upon the desired properties of the resins. The details of such a solution polymerization are disclosed in U.S. Patent No. 2,075,575, and the details of a suspension polymerization are described in U.S. Patent No. 3,172,877. These vinyl chloride/vinyl acetate copolymer resins have been used commercially mainly in the preparation of floor tiles.

It is also known that the copolymerization of vinyl chloride with ethylene or propylene offers an effective way to reduce the glass transition temperature of the copolymer with low levels of comonomer, and to increase flexibility for nonrigid applications. These olefins act as degradative chain transfer agents, thereby tending to retard the rate of polymerization of the vinyl chloride. Unless highly active initiators are used, the polymerization becomes very sluggish. The polymerization of vinyl chloride with ethylene is taught in U.S. Patent No. 3,501,440. The polymerization of vinyl chloride with propylene is described in U.S. Patent No. 3,468,859.

It is also known to copolymerize vinyl ethers with vinyl chloride to develop a material suitable as a surface coating applied as solvent solution, or to improve the

processability of polyvinyl chloride. The suspension and emulsion copolymerization techniques for making such copolymers can be found in U.S. Patent No. 3,168,594.

5 The incorporation of acrylates or acrylonitrile into vinyl chloride polymers modifies the properties and suitable end-use applications therefor. The copolymers with long chain acrylates provide a low glass transition temperature and improved adhesion and flexibility. The copolymers with acrylonitrile produce resins which are  
10 suitable for forming fibers and films. Most copolymerizations of vinyl chloride with acrylonitrile have been carried out via emulsion, as described in U.S. Patent No. 2,603,620. The chemically homogeneous copolymers of vinyl chloride with acrylates are difficult  
15 to synthesize due to the drastic difference in monomer reactivity ratios. U.S. Patent No. 3,230,206 teaches a technique for controlling the chemical heterogeneity of such a copolymer.

Functional groups have been incorporated into  
20 polyvinyl chloride resin, typically to make good protective coating materials. Those functional groups improve abrasion resistance and impart flexibility to the resins. U.S. Patent No. 2,147,154 discloses a method for binding carboxylic functional groups by polymerizing vinyl  
25 chloride with acrylic acid in emulsion. Hydroxyl functional groups have been brought into the polymer by polymerizing vinyl chloride with vinyl acetate and subsequently saponifying the copolymer, as described in U.S. Patent No. 2,852,499. Vinyl chloride has also been  
30 copolymerized with allyl alcohol and dibutyl fumarate, as disclosed in U.S. Patent No. 3,036,039. The mixture of allyl alcohol, vinyl chloride, and dibutyl fumarate was polymerized at 120°F in the absence of any solvent.

In U.S. Patent No. 3,632,542, a method is disclosed for copolymerizing vinyl chloride with ethylene and vinyl acetate. The resulting copolymers contained 5-25% ethylene, 10-35% vinyl chloride, and 40-85% vinyl ester.

5 These copolymers were purported to form films having good resistance to hydrolysis by aqueous alkali.

Mori et al. teach a method for preparing an interlayer film of a laminated safety glass in U.S. Patent Nos. 4,382,996 and 4,389,508. The film was prepared with

10 a thermoplastic resin composed of 80-98.5 weight percent vinyl chloride, 1-10 weight percent glycidyl methacrylate, and 0.5-10 weight percent ethylene. The interlayer was proclaimed to have superior penetration resistance, good handleability in bonding, and high bond strength.

15 In U.S. Patent No. 5,091,487, Hori et al. discuss an emulsion polymerization process for forming a vinyl chloride resin which is constituted of particles, each having a particle diameter of at most 5 $\mu$ m. The resin particles are formed of a copolymer comprising vinyl

20 chloride and an epoxy-containing monomer, wherein the epoxy content of the outer portion of the particle is higher than that of the inner portion thereof. While various polymerization processes are mentioned, all of the illustrative examples are of the emulsion polymerization

25 of vinyl chloride and glycidyl methacrylate. The vinyl chloride resin so formed is then included in a plastisol, which can be placed between two glass sheets and allowed to gel by heating to form a laminated safety glass. The resin obtained by the Hori et al. process, however, is not

30 suitable for use in a calendering or extrusion process, requires relatively high temperatures to obtain adequate adhesion, and appears to result in a safety glass having high haze.

Thus, in spite of all the progress made so far, vinyl chloride polymers having good heat stability, low haze, good adhesion and requiring low processing temperatures are yet to be developed.

5

#### SUMMARY OF THE INVENTION

This invention relates to a method for copolymerizing vinyl chloride with allyl glycidyl ether and a vinyl ester. In particular, the copolymers so formed consist of 10 70-99 weight percent of vinyl chloride, 0.05-15 weight percent of allyl glycidyl ether, and 0.05-15 weight percent of a vinyl ester, preferably vinyl acetate. Optionally, other copolymerizable monomers can be included up to 20 weight percent, but are preferably 10 weight 15 percent or less. Vinyl ethers are examples of such copolymerizable monomers which may advantageously be included. Alkyl vinyl ethers, such as octadecyl vinyl ether, are preferred.

The further copolymerization of the above three 20 monomers with low amounts generally of an unsaturated organic trifunctional silane provides self-adhesion without gelation along with other desirable properties such as low haze, low fisheye content and high plasticizer take up.

25 The copolymers of this invention can be compounded to provide films exhibiting improved heat stability, low haze, and good adhesion to solid surfaces such as glass and metal. The compounded resins thus obtained may be especially advantageously used in forming the interlayer 30 of laminated safety glazings, such as vehicle windshields and architectural glazings.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to the copolymerization of vinyl chloride with allyl glycidyl ether and a vinyl ester, optionally in the presence of one or more other  
5 copolymerizable monomers. It is believed that the inclusion of the vinyl ester results in improved adhesion. It is also believed that the presence of allyl glycidyl ether imparts improved heat stability to the polymers, and also provides improved adhesion beyond that which is  
10 provided by the inclusion of vinyl ester alone. The combination of allyl glycidyl ether with the vinyl ester also provides unexpectedly low haze. The polymers of this invention are aimed at being compounded to make films with good heat stability, low haze, and good adhesion. It is  
15 noted that the polymers which show good heat stability also exhibit good light stability.

It is possible to produce the polymers of this invention by suspension polymerization, emulsion polymerization, or solution polymerization. However, when  
20 the polymers are intended for use in applications requiring low haze, good adhesion, and low processing temperatures, suspension polymerization is by far preferred. The high surfactant level used in emulsion polymerization interferes with adhesion. In addition, the  
25 relatively small particle size of the polymer resulting from emulsion polymerization prevents processing via calender or extrusion, limiting further processing to plastisol fusion requiring thermoforming process temperatures which are higher than desirable for many  
30 applications, including the formation of a safety glass laminate. Solution polymerization is inappropriate for many applications since the molecular weight of the resulting polymer is limited to levels which are lower



than desired. There are also environmental and cost concerns associated with solution polymerization.

#### Monomer

5       The copolymers of this invention are produced by polymerizing at least three monomers. Additionally, other copolymerizable monomers may be incorporated into the polymers. The level of vinyl chloride is kept at from about 70 weight percent up to 99 weight percent. The  
10       suitable content of allyl glycidyl ether is at least 0.05% by weight. If the amount of allyl glycidyl ether exceeds 15%, the molecular weight of the copolymers will likely be too low, resulting in a polymer having insufficient tensile and impact strengths for many applications. In  
15       order to minimize gelation that may occur with excess allyl glycidyl ether alone, and hence to impart sufficient processability and adhesion of the polymers to solid surfaces such as metal and glass, the copolymers ought to have at least 0.05 weight percent of a vinyl ester.  
20       Suitable vinyl esters include vinyl acetate, vinyl propionate, etc., with vinyl acetate being preferred.

      The adhesion of the copolymers can also be boosted significantly with the addition of proper kinds of silane compounds during the polymerization or at the compounding  
25       stage. If more than 15 weight percent of vinyl ester is included, the colloidal stability during polymerization is adversely affected, the drying of the polymers becomes unusually difficult, and the resulting polymers have a porosity which is too low to absorb the additives  
30       satisfactorily during compounding.

      Other copolymerizable comonomers include monomeric esters such as ethyl acrylate, methyl methacrylate,

glycidyl methacrylate, hydroxyethyl (meth)acrylate, etc.; monomeric ethers such as isobutyl vinyl ether, trimethylolpropane monoallyl ether, diallyl ether, octadecyl ether, etc. olefins such as ethylene, propylene, etc.; monomeric hydrocarbons such as styrene,  $\alpha$ -methyl styrene, etc.; acrylonitrile; monomeric amines such as 2-vinylpyridine, allyldimethylamine, etc.; monomeric silanes such as vinyltriacetoxysilane,  $\gamma$ -methacryloxy propyl trimethoxysilane, etc.; monomeric ketones such as methyl vinyl ketone,  $\alpha$ -acetoxystyrene, etc; and so on.

#### Solvent

In suspension polymerization, the solvent is usually deionized water. A minor amount of hydrocarbon or polar solvent, such as hexane or methanol, can be added to facilitate homogeneous dispersion of the initiators. The usage level of the deionized water is preferably equal to or higher than 100 parts per hundreds of monomers (phm).

#### Initiator

In accordance with the process of this invention, initiators are used which are miscible with hydrocarbon solvents. Examples of those initiators include diacyl peroxides such as lauroyl peroxide, benzoyl peroxide, etc.; peroxydicarbonates such as di(2-ethylhexyl) peroxydicarbonate, di(sec-butyl) peroxydicarbonate, etc.; peroxyesters such as t-butyl peroxyneodecanoate, t-butyl peroxy-pivalate, etc.; peroxides such as acethylcyclohexylsulfonyl peroxide, 3,4,5-trimethylhexanoyl peroxide, etc.; azo compounds such as azobis, 2,4-dimethyl valero nitrile, azobis

(4-methoxy-2,4-dimethylvaleronitrile), etc.; and so on. As an option, initiators miscible with water may be used as well.

The initiators may be used singly or in combinations  
5 of two or more to keep the level of free radicals steady throughout the polymerization. Generally, the initiator or initiator mixture is used in an amount in the range of about 0.01 to 0.5 phm. In the case of a fast  
polymerization, or extremely low molecular weight polymer,  
10 initiators in an amount higher than 0.5 phm may be used, if the heat of polymerization can be handled adequately.

#### Emulsifier

This invention does not impose any restriction on the  
15 choice of emulsifiers. Any dispersant used in the trade is usable. Examples of suitable emulsifiers include water-soluble cellulose esters such as hydroxypropylmethyl cellulose, hydroxyethyl cellulose, etc.; water-soluble  
polymers such as partially saponified polyvinyl alcohols,  
20 polyacrylic acid, gelatin, etc.; non-ionic surfactants such as sorbitan monolaurate, polyethyleneoxide sorbitan stearate, etc.; and so on. These emulsifiers are frequently used in combination of two or more to enhance the stability of the suspension droplets formed by  
25 agitation and balance the properties of the resin at the same time. The preferred level of the emulsifiers is about 0.03 to 0.5 phm.

#### Short-stopping Agent

30 The polymerization is terminated when the vinyl chloride conversion into polyvinyl chloride is in the range of from about 50% to 90%. The polymerization is

usually terminated with the addition of short-stopping agents or stabilizers which inhibit polymerization. An exemplary stabilizer is a sulfur-containing organo-tin stabilizer, especially di-n-butyl tin, S,S'-bis-(isooctyl mercaptoacetate), as well as organo phosphite, and mixed salts thereof. Other exemplary short-stopping agents include  $\alpha$ -methyl styrene, hydroquinone, bisphenol-A; thioalcohols; acetone thiosemicarbazone; and amines. The short-stopping agent is preferably used in amounts ranging from about 0.005 phm to about 2 phm.

#### Other Additives

Other additives may be added to the aforementioned ingredients for polymerization in accordance with this invention. Examples of such other additives include scale inhibitors such as nitric acid, oxalic acid, etc.; defoamers such as dimethyl silicones, ethylene oxide-propylene oxide block polymers, etc.; chain transfer agents such as trichloroethylene, mercapto ethanol, etc.; chelating agents such as diethylene triamine pentaacetic acid, ethylene diamine tetraacetic acid, etc.; and so on. Other additives which may be incorporated include the family of tri-alkoxy organofunctional silanes which can act as defoamers and as adhesion promoters or coupling agents in subsequent compounding and in the end use of the final resin. These silane coupling agents can be of the vinyl functional type and can thus be chemically copolymerized, or they can be of other types which can be introduced during the polymerization or post-polymerization to the slurry prior to drying. These additives can be added in any suitable amount, as is known by those skilled in the art.

### Suspension Polymerization

The suspension polymerization in accordance with the invention can be carried out batchwise or semibatchwise. Semibatch is usually preferred in order to achieve a  
5 homogeneous composition of copolymers when the reactivity ratios are quite different. Predominately, batch polymerization is utilized due to its simplicity and low cost of operation. In a batch polymerization, all of the ingredients are charged into a clean reactor before the  
10 on-set of polymerization. The reactor can be fabricated with stainless steel or can be clad with glass. Subsequent to the charge of all ingredients, the reactor is heated up to a predetermined temperature in the range of 40°C to 80°C with adequate agitation. The consideration  
15 of conversion and porosity determines the allowance for the total polymerization time, which is generally in the range of from 3 hours to 15 hours. The polymerization is terminated with a proper kind of short-stopping agent when the pressure in the reactor head space drops to the  
20 predetermined level coinciding with the targeted degree of conversion. Thereafter, the slurries, which are formed through the phase change of liquid monomer droplets to discrete solid particles, are transferred to a stripping column, where the residual monomers are stripped from the  
25 resin particles by subjecting the slurries to steam under vacuum. The steam-stripped slurry is then sent to a dryer through a centrifuge.

### Resin Characterization

The resins were characterized by seven measurements: degree of polymerization, bulk density, plasticizer absorption, average particle size, fish eyes, haze, and  
5 heat stability.

Degree of polymerization was determined according to Japanese Industry Standard ("JIS") K-6721-1977.

Bulk density is the weight per unit volume of PVC including voids inherent in the PVC. The unit is g/cc.  
10 These test methods provide useful indexes of performance of plastic materials with respect to their handling in packaging and fabrication. The bulk density is a measure of the fluffiness. The procedure for determining bulk density is well described in ASTM D1895-89(1990).

15 Plasticizer absorption (plasticizer take-up) was determined according to ASTM D3367 (75)-1990. The test method covers determination of the plasticizer absorption of PVC using a controlled centrifugal force. Plasticizer absorption of the test sample is reported in percentage.

20 The measurements for average particle size followed the procedure in ASTM D1921-89. The test methods cover the measurement of the particle size of plastic materials in the powdered granular or pelleted forms in which they are commonly supplied.

25 The procedure in ASTM D3592-92 is used for determination of fisheyes in PVC homopolymer resins and similar resins. The presence of fisheyes in a film or sheet lower the product quality. The number of clear, undyed spots in a sheet of 100 cm<sup>2</sup> is counted as the  
30 number of fisheyes. The sample resin, mixed with the plasticizer, stabilizer, and colorant, is milled on a hot

roll. A sheet with constant thickness is formed under fixed conditions.

The degree of haze, or wide angle diffuse scattering of light, was determined by following the procedure described in ASTM D1003. The specimens were prepared by a sequence of roll milling and hot pressing. The specimens were roll milled at 190°C for 5 minutes. The operation conditions for hot pressing were to keep the specimens at 180°C for 5 minutes for pre-heating, at 180°C for 5 minutes under 100 kg/cm<sup>2</sup>, and then at 25°C for 3 minutes cooling. The specimen size was 80mm x 45mm x 3.2mm. The measurements were done with a Model SM-6 hazemeter made by Suga Test Instrument Co. using an illuminate C source of light. The degree of haze was reported in percentage.

The method used to determine the heat stability of each specimen was as follows. A specimen was prepared with a twin mill made by Nishimura of Japan. The roll surface temperature was kept at 145°C. The specimen was then subjected to rolling for 5 minutes and 30 seconds. The thickness of the specimen was 0.7mm. The formulation compounded for the specimens was 100 parts per hundred parts resin ("phr") of the vinyl chloride polymer resin, 40 phr dioctyl phthalate ("DOP"), 2 phr of a liquid tin stabilizer (Stabilizer BC 747 available from Ciba-Geigy), and 0.3 phr stearic acid as a lubricant. The specimen sheet coming out of the twin roll mill was then cut into a 450mm x 30mm x 0.7mm specimen strip. The specimen strip was placed in a Mathis Thermotester, Model LTF-ST-152293 manufactured by Werner Mathis of Switzerland. The Thermotester oven was kept at 185°C with a strip moving pace of approximately 19mm/5 minutes. The time taken for the specimen strip to be discolored to black is reported in minutes.

A specimen with the size, 70mm x 70mm x 0.7mm was prepared from the sheet made to test the adhesion. The specimen was inserted between two glass plates of 70mm x 70mm x 0.7mm, and put into an oven for 10 minutes. The temperature of the oven was kept at 200°C. The rating was classified as poor or good by the effort required to separate the specimen from the glass plate.

#### Product Applications

The polymers which are produced by the method in accordance with this invention can be used to fabricate films with improved heat stability, low haze, and good adhesion. The polymers of this invention have a degree of polymerization of at least about 400, and preferably at least about 530. A degree of polymerization lower than about 400 will result in a loss of mechanical properties, such as impact resistance, in the final product. For certain applications, such as for forming an interlayer for a laminated safety glazing, the polymers of this invention preferably have a degree of polymerization of at least about 900.

The polymers of this invention also have an average of particle size of at least about 10 $\mu$ m, and preferably at least about 30 $\mu$ m. If the average particle size is less than about 10 $\mu$ m, then the films formed therewith generally exhibit high haze and the porosity of the particles is disadvantageously low, resulting in difficulties in compounding. On the other hand, if the average particle size is greater than about 250 $\mu$ m the porosity may again be so low that difficulties in compounding are experienced.

As noted above, use of these polymers is especially advantageous in the formation of interlayers for laminated



safety glazings, which are composed of an interlayer bonding together two glass plates or sheets so that breaking the glass results in minimum dispersion of broken glass fragments. Such an interlayer must possess a number of properties, including: high impact energy adsorption to minimize concussive injury; shear and tear strength sufficient to prevent rupture of the interlayer by the broken glass; sufficient adhesion to the glass to inhibit laceration on contact with, and prevent dispersion of, broken glass; acceptable thermal heat stability and weatherability; and good optical quality after processing the laminates with conventional equipment such as pre-presses and autoclaves at temperatures as low as 140°C. The interlayer must possess and maintain these properties over the wide range of temperatures in which these laminated glazings are used.

Certainly, the polymers of this invention can be used in many other applications for high performance flexible resins as well.

#### EXAMPLE 1

The following examples are illustrative of the invention and do not constitute any limitation with regard to the subject matter of the invention. Six different specimens are compiled. Two of them are controls which are used to compare with the four polymers made by the method of this invention.

The polymerization was carried as follows:

1. The inner surfaces of reactor were cleaned thoroughly. The volume of the reactor was 1 m<sup>3</sup>. The reactor was equipped with a Pfaudler agitator, 2 cooling baffles, and a condenser.

2. The inner surfaces of the reactor were coated with a scale inhibitor.

3. The deionized water was charged to the reactor and an agitator activated.

5        4. The emulsifiers and all other additives were charged to the reactor.

5. The initiators were added.

6. Mixing was maintained for 30 minutes, while the vacuum was pulled down to 30 mm Hg.

10       7. The monomers were then added. The total amount of vinyl chloride charged into the reactor wads 280 kg. Accordingly, the quantities of other ingredients were adjusted.

15       8. The polymerization temperature was maintained at 53°C.

9. The polymerization was terminated with the addition of 0.04 phm of Bisphenol-A, when the head space pressure reached 90 psi.

20       10. The slurry was then transferred from the reactor to a stripping column.

Various resin compositions and the resulting characteristics of each resin are presented at Table 1. All of the amounts listed in Table 1 are in weight percent unless otherwise indicated. Control A was chosen to see  
25 whether an acrylic monomer with an epoxy group could provide the desired properties. The test results show that, while adhesion to a glass surface was good, the polymer with glycidyl methacrylate and vinyl acetate  
30 exhibits a high level of fisheyes, high haze, and poor heat stability. Control B was selected to see whether vinyl acetate alone provide the properties needed for high performance films. The polymer with vinyl acetate also

exhibited high haze and poor heat stability. In addition, adhesion to a glass surface was poor. Consequently, Control A and B were not acceptable for applications requiring the properties noted above, such as for a safety glass interlayer.

The test data from P1 to P4 illustrate the simultaneous presence of allyl glycidyl ether and vinyl acetate in the polymers provide the physical properties needed for the film. Those polymers indeed have low haze and excellent heat stability in comparison with control resins. Those resins also showed good adhesion to a glass surface. Furthermore, it can be seen that optional presence of other copolymerizable monomers can be quite beneficial. For example, 3 parts of trimethylolpropane monoallyl ether increased the heat stability significantly, and 0.4 parts of octadecyl vinyl ether reduced the fisheyes to zero. The copolymers of vinyl chloride in the range of 70 weight percent to 99 weight percent with 0.05-15 weight percent of allyl glycidyl ether and 0.05-15 weight percent of vinyl acetate will perform quite well as a thermoplastic resin which can be compounded to prepare films with excellent heat stability, low haze, and good adhesion. A judicious choice of other copolymerizable monomer(s) will further the properties of the resins advantageously. A presence of a proper kind of silane compound will augment the adhesion strength to glass surfaces. Those same copolymers can also be used as the binder for ferrite powders with a proper compounding; as a binder for other types of metal or metal oxide powders for magnetic tape applications; and even as a coating for aluminum containers or sheets.

TABLE 1

	Control A	Control B	P1	P2	P3	P4
Vinyl Chloride	100	100	100	100	100	100
Deionized Water	150	150	150	150	150	150
Initiator	0.35	0.35	0.35	0.35	0.35	0.35
Emulsifiers	0.144	0.144	0.144	0.144	0.144	0.144
Glycidyl methacrylate	3	-	-	-	-	-
Allyl glycidyl ether	-	-	3	1	3	3
Vinyl acetate	1	3	0.5	1	1	1
Octadecyl vinyl ether	-	-	-	0.4	-	0.4
Trimethylol- propane monoallyl ether	-	-	-	-	3	-
Degree of polymerization	800	1150	550	730	530	610
Bulk density (g/cc)	0.46	0.54	0.58	0.56	0.59	0.48
PTU (%)	10	12	10	12	11	21
Average particle size ( $\mu\text{m}$ )	200	175	150	152	250	85
Fisheyes	250	55	40	0	75	0
Haze (%)	12	10	1	1.7	2	1
Heat stability (minutes)	45	40	90	75	100	90

Initiator: Di(2-ethylhexyl) peroxydicarbonate

Emulsifiers: Polyvinyl alcohol with 72.5%  
hydrolysis 0.072; Polyvinyl alcohol  
with 40% hydrolysis

Fisheyes: Number of gels/100 cm<sup>2</sup>

PTU: Plasticizer take-up (plasticizer  
absorption)

EXAMPLE 2

In order to test the resin for use in laminated safety glass applications, samples were dry blended with a range of plasticizer and stabilizer combinations, and were  
5 then milled at a roll temperature of approximately 300 °F for 7 minutes. The milled films were then laminated between two sheets of 0.088" flat glass using an autoclave at 300 °F and 240 psi for 45 minutes. The laminates were then tested for haze, yellowness index, pummel adhesion,  
10 and thermal stability as a function of time at 100 °C. These results are shown in Table 2.

As shown by these examples, the copolymers of this invention can be used to make interlayers for safety glass laminates that simultaneously exhibit low haze, good  
15 thermal stability, and good adhesion to glass without the need for the undesirably high process temperatures required of plastisol type or polyvinyl chloride homopolymer resins.

TABLE 2

	Component	A (phr)	B (phr)	C (phr)
	P4	--	95	--
5	P1 resin	92	--	95
	CAPA 650 <sup>1</sup>	8	5	5
	n-octyl decyl adipate (NODA)	36	17	17
	dihexyl adipate (DHA)	4	17	17
10	Drapex 6.8 <sup>2</sup>	5	5	5
	Meister CZ5062 <sup>3</sup>	3	--	--
	UBZ 7910 <sup>4</sup>	--	3	3
	Tinuvin 328 <sup>5</sup>	0.2	0.2	0.2
	CPL-46 <sup>6</sup>	0.1	0.1	0.1
15	Irganox 1010 <sup>7</sup>	0.5	0.5	0.5
	Y9669 <sup>8</sup>	0.75	1	0.1
	Haze	0.6	0.6	0.6
	Pummel	10	4	3
20	ΔYI <sub>c</sub> after 500hrs at 100° C	4	4	3

1. Polycaprolactone resin available from Solvay Interlox.

2. Epoxidized soybean oil available from Witco Corp. of Oakland, NJ.

3. Calcium zinc stabilizer available from Meister of Switzerland.

4. Barium/zinc stabilizer package available from Baerlocher USA of Dover, OH.

5. Benzotriazole ultraviolet light stabilizer available from Ciba-Geigy Corp.

6. Perchlorate stabilizer available from Asahi Denka Kogyo K.K. of Japan.

5 7. Hindered phenolic antioxidant available from Ciba-Geigy Corp.

8. Phenylaminopropyl trimethoxysilane available from OSi, Inc.

10 It has been found that very low amounts (0.1 or 0.2 to 0.8 weight percent) of an unsaturated organic trifunctional silane can be used for copolymerization with vinyl chloride, allyl glycidyl ether, and a vinyl ester. The resultant copolymer has self-adhesion and can be made  
15 with no gelation. Desirable properties of low haze, low fisheye content, good heat stability, good UV stabilization, and good plasticizer take-up are maintained or improved. The copolymers with silane were prepared as set forth in the preceding Examples except that a small  
20 amount (preferably about 0.5% by weight) of the silane was used, generally added a short time after the other monomers were charged into the reactor.

The silane copolymer was used as the interlayer for a laminated safety glazing and other product applications  
25 set forth for the polymers without the silane.

An effective self-adhesion promoting amount (and a non-gelling amount) of silane (about 0.5%, by weight) of the preferred silane that is  $\gamma$ -methacryloxy propyl trimethoxysilane is used.

30

### EXAMPLE 3

Results of tests using the unsaturated organo silane are shown in Table 3.

TABLE 3

	Control	P1	P2	P3	P4	P5
5	Vinyl Chloride	100	100	100	100	100
	Deionized water	150	150	150	150	150
	Initiator	0.35	0.35	0.35	0.35	0.35
	Emulsifiers	0.144	0.144	0.144	0.144	0.144
	Allyl glycidyl ether	1	2	3	2	1
10	Vinyl acetate	1	0.5	0.5	-	0.5
	Methyl acrylate	-	-	-	2	-
	Octadecyl vinyl ether	0.4	0.05	-	0.05	0.05
	Vinyl triacetoxysilane	-	-	0.5	-	-
	$\gamma$ -methacryloxy propyl trimethoxysilane	-	0.5	-	0.5	0.5
15	Trimethylolpropane monoallyl ether	-	-	1	-	-
	Degree of polymerization	730	840	640	880	1020
20	Bulk density (g/cc)	0.58	0.52	0.44	0.49	0.37
	PTU (%)	12	21.6	113	88	75.2
	Average particle size ( $\mu$ m)	152	80	113	88	110
	Fisheyes	0	3	30	120	5
25	Haze (%)	1.7	2	2	2	2
	Heat stability (minutes)	75	80	80	80	75
	Self-adhesion	No	Yes	Yes	Yes	Yes
30	Initiator	Dl-(2-ethylhexyl) peroxydicarbonate				
	Emulsifiers	Polyvinyl alcohol with 72.5% hydrolysis				
		Polyvinyl alcohol with 40% hydrolysis				
35	Fisheyes	Number of gels per 100 cm <sup>2</sup>				
	PTU	Plasticizer take-up (plasticizer absorption)				



A further test (P6) in the P1 to P5 tests series shown in Table 3 was conducted as follows:

		P6
5	Vinyl chloride	100
	Deionized water	150
	Initiator	0.35
	Emulsifiers	0.144
	Allyl glycidyl ether	2
10	Vinyl acetate	0.5
	Methyl acrylate	-
	Octadecyl vinyl ether	0.05
	Vinyl triacetoxysilane	-
15	$\gamma$ -methacryloxy propyl trimethoxysilane	0.6
	trimethylolpropane monoallyl ether	-
	Degree of polymerization	850
	Bulk density (g/cc)	.609 g/cm <sup>3</sup>
20	PTU (%)	22.4
	Average particle size ( $\mu$ m)	108 $\mu$ m
	Fisheyes	0
	Haze (%)	-
	Heat stability (minutes)	-
25	Self-adhesion	Yes

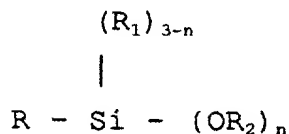
The tests P5 and P6 with  $\gamma$ -methacryloxy propyl trimethoxysilane provides superior results, the silane being highly preferred.

30 The range of silane used is about 0.1 weight percent or 0.2 or 0.3 (the lowest level is determined by the minimal amount needed to give some adhesion) up to 0.7 or

0.8% by weight being the maximum (or as determined by the onset of gelation and fisheyes). The preferred amount of the preferred silane is about 0.5 to 0.6% by weight.

Other useful silanes are trifunctional (alkoxy) silanes having an unsaturated organic radical having 2 to 10 or 12 carbon atoms. Useful trifunctional silanes include those with vinyl or allyl groups such as vinyl trialkoxysilane and allyl trialkoxy silane.

Although not as useful as the above-described superior silanes and trifunctional silanes, a silane of the following formula can be used in some applications:



where n is 1 to 3;

where R is an unsaturated organic radical containing a double bond and generally C atoms and O atoms in the chain; and

where R<sub>1</sub> is an alkyl such as ethyl, methyl, propyl and butyl.

The upper limit of these would be higher than the 0.7 or 0.8% of the preferred silanes, in some cases, such cross linking and gelation/fisheyes are less frequent with n < 3.

The great benefits of self-adhesion without gelatin is obtained by the use of an effective self-adhesion promoting amount (and effective non-gelling amount) of the silane. The above effective amount is equivalent to the use of about 0.5% by weight of  $\gamma$ -methacryloxy propyl trialkoxy silane as shown, for instance in tests P5 and P6 of Example 3 (Table 3).

The novel silane/vinyl chloride/allyl glycidyl ether/vinyl acetate copolymer can be blended with an acrylic resin tackifier for further improving the adhesion to glass. The reaction product of an acrylic resin and an  
5 organic unsaturated alkoxy functional silane can also be used as an effective tackifier.

## WHAT IS CLAIMED IS:

1. A process for making a vinyl chloride copolymer resin comprising suspension polymerizing a monomer mixture in a process wherein water is the continuous phase and the monomer mixture is the discontinuous phase, said monomer mixture including at least about 70% by weight vinyl chloride, from about 0.05% by weight to about 15% by weight allyl glycidyl ether, from about 0.05% by weight to about 15% by weight of a vinyl ester, and an effective self-adhesion prompting without gelling amount of an unsaturated organic alkoxy functional silane that is equivalent to about 0.5% by weight of  $\gamma$ -methacryloxy propyl trimethoxysilane.

2. A process as defined in claim 1, wherein said vinyl ester is vinyl acetate.

3. A process as defined in claim 1, wherein said monomer mixture further includes an allyl ether or mixture of allyl ethers, the amount of which does not exceed about 20% by weight of said total monomer mixture.

4. A process as defined in claim 3, wherein said allyl ether is trimethylolpropane monoallyl ether.

5. A process as defined in claim 1, wherein said monomer mixture further includes a vinyl ether, the amount of which does not exceed about 20% by weight of said total monomer mixture.

6. A process as defined in claim 5, wherein said vinyl ether is an alkyl vinyl ether.

7. A process as defined in claim 6, wherein said  
5 vinyl ether is octadecyl vinyl ether.

8. A process as defined in claim 1, wherein the amount of water is equal to or greater than 100 parts by weight of the monomer mixture.

10

9. A vinyl chloride copolymer constituted of particles prepared by the suspension polymerization of a monomer mixture comprising:

(a) vinyl chloride or a mixture of vinyl chloride  
15 and one or more other vinyl monomers copolymerizable therewith; and

(b) allyl glycidyl ether;

(c) a vinyl ester; and

(d) an unsaturated organic alkoxyfunctional silane  
20 wherein the average particle size of said polymer particles is between about 10 $\mu$ m and about 250 $\mu$ m.

10. A vinyl chloride copolymer as defined in claim 9, wherein the average particle size of said polymer  
25 particles is between about 30 $\mu$ m and about 250 $\mu$ m.

11. A vinyl chloride copolymer as defined in claim 10, wherein the average particle size of said polymer particles is at least about 85 $\mu$ m.

30

12. A vinyl chloride copolymer as defined in claim 9 which is prepared by the suspension polymerization of a monomer mixture including at least about 70% by weight vinyl chloride, from about 0.05% by weight to about 15% by weight allyl glycidyl ether, and from about 0.05% by weight to about 15% by weight of a vinyl ester.

13. A vinyl chloride copolymer as defined in claim 9, wherein the degree of polymerization of said copolymer is at least about 400.

14. A vinyl chloride copolymer as defined in claim 13, wherein the degree of polymerization of said copolymer is at least about 530.

15. A vinyl chloride copolymer as defined in claim 14, wherein the degree of polymerization of said copolymer is at least about 800.

16. A laminated glazing unit, comprising a first glass sheet, a second glass sheet and an interlayer adhered therebetween, said interlayer being formed of a film including a vinyl chloride copolymer formed by the suspension polymerization of a monomer mixture including vinyl chloride, allyl glycidyl ether, a vinyl ester, and an unsaturated organic alkoxy functional silane that provides self-adhesion without gelation.

17. A laminated glazing unit as defined in claim 16, wherein said vinyl chloride copolymer is prepared by the suspension polymerization of a monomer mixture including at least about 70% by weight vinyl chloride, from about  
5 0.05% by weight to about 15% by weight allyl glycidyl ether, from about 0.05% by weight to about 15% by weight of a vinyl ester, and no more than about 0.8% by weight of an unsaturated organic trifunctional silane.

10 18. A laminated glazing unit as defined in claim 17, wherein said vinyl ester is vinyl acetate.

19. A laminated glazing unit as defined in claim 16, wherein said monomer mixture further includes an allyl  
15 ether or mixture of allyl ethers, the amount of which does not exceed about 20% by weight of said total monomer mixture.

20. A laminated glazing unit as defined in claim 19, wherein said allyl ether is trimethylolpropane monoallyl  
20 ether.

21. A laminated glazing unit as defined in claim 16, wherein the degree of polymerization of said copolymer is  
25 at least about 530.

22. A laminated glazing unit as defined in claim 21, wherein the degree of polymerization of said copolymer is at least about 900.

23. A laminated glazing unit as defined in claim 16, wherein said interlayer, when formed as a film of nominal thickness of about 30 mils and laminated between a pair of glass sheets each having a nominal thickness of about 88  
5 mils, having a pummel value of at least 3 and a haze value of less than 1%.

24. A process as defined in claim 1, in which the silane is  $\gamma$ -methacryloxy propyl trimethoxysilane.  
10

25. A process as defined in claim 1 in which the silane is vinyl trialkoxysilane.

26. A vinyl chloride copolymer as defined in claim  
15 9, in which the silane is  $\gamma$ -methacryloxy propyl trimethoxysilane.

27. A vinyl chloride copolymer as defined in claim  
20 9, in which the silane is  $\gamma$ -methacryloxy vinyl trimethoxysilane.

28. A laminated glazing unit as defined in claim 16, in which the silane is  $\gamma$ -methacryloxy propyl trimethoxysilane.  
25

29. A laminated glazing unit as defined in claim 16, in which the silane is  $\gamma$ -methacryloxy vinyl trimethoxysilane.  
30



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/17268

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 14/06, 224/00  
US CL : 526/273, 320, 344, 332

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/273, 320, 344, 332

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,178,423 A (ANDERSON et al.) 11 December 1979.	1-29
A	US 3,928,684 A (BUNING et al.) 23 December 1975.	1-29

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 DECEMBER 1997

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26 JAN 1998

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JEFFREY T. SMITH

Telephone No. (703) 308-2351